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Markovnikov-selective Palladium Catalyst for Carbonylation of Alkynes with Heteroarenes

Jie Liu, Haoquan Li, Ricarda Dühren, Jiawang Liu, Anke Spannenberg, Robert Franke, Ralf Jackstell, and Matthias Beller*

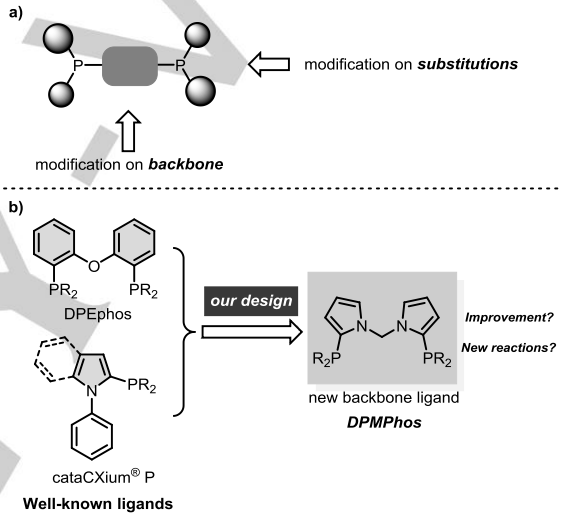
Dedication to Professor Dr. Lutz-Friedjan Tietze on the occasion of his 75th birthday.

Abstract: A new class of palladium catalysts based on heterocyclic diphosphines are rationally designed and synthesized. Application of one of these catalysts allows for novel Markovnikov-selective carbonylation of non-activated alkynes with heteroarenes to give the corresponding branched α,β-unsaturated ketones in excellent yields (up to 97%) and regioselectivities (*b:l* up to 99:1). In addition to heteroarenes, other common nucloephiles (alcohol, phenol, amine and amide) furnish the desired carbonylation products smoothly in high yields.

The development of ligands plays a key role in enabling new transformations and fine-tuning the chemo- or regioselectivity in homogenous catalysis. Illustrative examples include polymerizations, cross-coupling reactions, carbonylations, hydrogenations and metathesis.[1] Although a plethora of nitrogen- and phosphorous-based ligands have been developed over the last decades, their rational design to afford highly active catalyst systems, which can be easily prepared and modified, continues to be an important topic in this area.[2]

Among the privileged ligand classes known, especially bi- and multidentate derivatives create highly stable and selective organometallic complexes.[3] In these cases, properties and performance can be varied by changing either the ligand backbone or the substituents on the donor (e.g. phosphorus or nitrogen) atoms through steric and electronic effects (Scheme 1a).[4] Inspired by the valuable DPEphos ligand[5] and pyrrole-based monophosphines (cataCxium® P series) in various carbonylative transformations and cross-coupling reactions,[6] we had the idea to design diphosphine ligands containing *N,N'*-dipyrrolylmethane backbone (Scheme 1b). Advantageously, we expected these novel ligands to be conveniently prepared in two-steps. Variation of the heterocycle and the phosphine building blocks should generate related derivatives in a highly modular manner.

Carbonylation reactions belong to the most important industrial applications in the area of homogeneous catalysis and a variety of value-added bulk and fine chemicals are available via this technology.[7] Since the original work of Reppe in the past century,[8] carbonylation of alkynes with various nucleophiles such as H_2O,[9] alcohols (*O*-nucleophiles),[10] thiols (*S*-nucleophiles)[11] and amines (*N*-nucleophiles)[12] have been extensively studied and numerous catalysts are available for producing all kinds of carbonyl compounds. On the other hand,



Scheme 1. a) Ligand modification and b) design of DPMPhos ligands.

the use of *C*-nucleophiles which creates synthetic important ketones has been investigated to a lesser extent. In fact, only one example utilizing indoles as *C*-nucleophiles in alkyne carbonylation reactions has been reported by Alper and co-workers and this methodology is limited to activated alkynes.[13] To the best of our knowledge, Markovinkov selective carbonylations of alkynes with heteroarenes are unknown, even though the potential products that would arise from such reactions have broad utility in organic synthesis. In this respect, we report herein our recent investigations on the development of a general and efficient palladium catalyst for the Markovinkov-selective carbonylation of unactivated alkynes.

Some years ago, we reported the synthesis of 1-arylpyrrolyl- and –indolyl-2-phosphines, which have been also commercialized (cataCxium® P series).[6a] Notably, these ligands can be easily prepared by deprotonation at the α-position of the heterocycle, thus allowing an efficient modular synthesis of all kinds of related derivatives. In order to take advantage of this activation for the generation of bidentate ligands, we had the idea to use *N,N'*-dipyrrolylmethanes as a new scaffold. Indeed, without pre-halogenation of *N,N'*-dipyrrolylmethanes, ligands **L1** and **L2** can be smoothly synthesized via directly lithiation with

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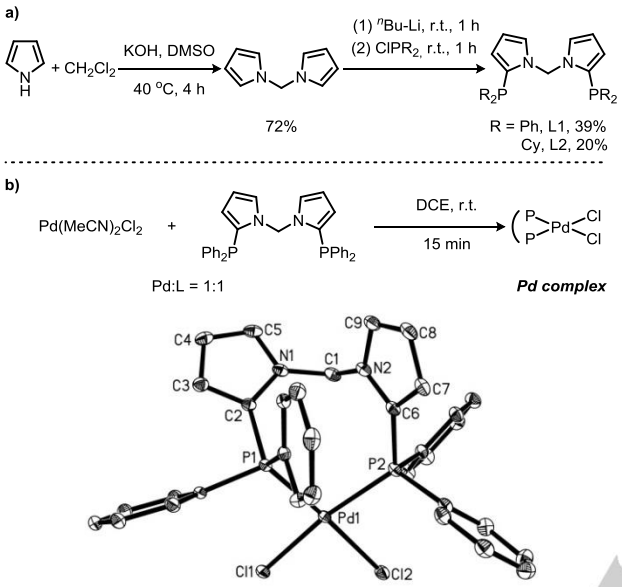
two equivalent of ^{n}BuLi and subsequent coupling with chlorodiphenylphosphine and chlorodicyclohexylphosphine, respectively (Scheme 2a). A palladium complex was obtained by treating **L1** with $Pd(MeCN)_2Cl_2$ in 1,2-dichloroethane. The structure of Pd(**L1**)Cl_2 was confirmed by X-ray crystallography (Scheme 2b).[14]



Scheme 2. a) Preparation of bis(2-(diphenylphosphanyl)-1H-pyrrol-1-yl)methane; b) molecular structure of Pd(**L1**)Cl_2 in the crystal. Displacement ellipsoids correspond to 30% probability. Hydrogen atoms and co-crystallized solvent are omitted for clarity.

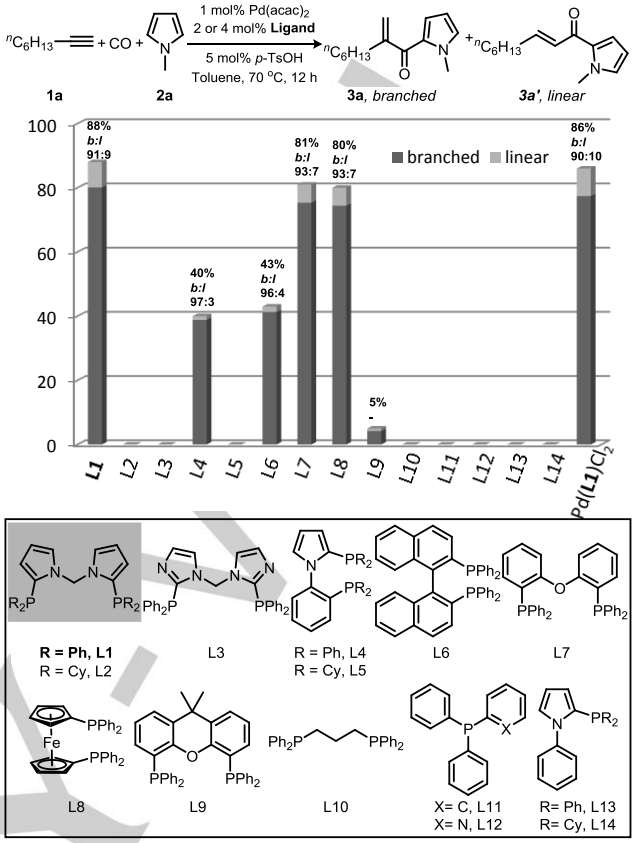


Figure 1. Ligand effect for Markovnikov-selective carbonylation of **1a** with **2a**. Reaction conditions: **1a** (1.0 mmol), **2a** (0.5 mmol), $Pd(acac)_2$ (1.0 mol%), bidentate ligand (2.0 mol%) or monodentate ligand (4.0 mol%), *p*-TsOH (5.0 mol%), CO (40 bar), toluene (1.0 mL), 70 °C, 12 h. Yields (**3a** and **3a'**) and regioselectivities were determined by GC analysis using isooctane as the internal standard.

With the new phosphine ligands in hand, the carbonylation of 1-octyne **1a** with *N*-methylpyrrole **2a** was investigated. We observed a high yield (88%) and good selectivity (*b*/*l* = 91:9) for the desired α,β-unsaturated ketone **3a** in the presence of **L1** (bis(2-(diphenylphosphanyl)-1H-pyrrol-1-yl)methane). However, **L2** bearing the electron-rich dicyclohexylphosphino groups, suppressed this reaction. Similarly, using the imidazolyl-based ligand **L3**, no desired product was obtained. Among the known diphosphines with aryl-(hetero)aryl backbones **L4**-**L6**, **L4** and *rac*-binap **L6** showed moderate reactivity. In contrast, applying DPEphos **L7** and dppf **L8** led to high yields of **3a** (81% and 80%, respectively), while the more rigid ligand Xantphos **L9** gave much worse result. Other bidentate phosphine **L10** and common monodentate ligands such as PPh_3 **L11**, PPh_2Py **L12**, cataCxium® P series **L13** and **L14** all exhibited no activity for this carbonylation process. As expected, compared to the *in situ* system using the defined Pd(**L1**)Cl_2 complex led to the desired product in comparable yield (86%) and good regioselectivity (*b*/*l* = 90:10).

After optimizing the reaction conditions (see Supporting Information, Tables S1), we explored the general applicability of our novel catalyst and the substrate scope. Here, at first reactions of various alkynes **1** with *N*-methylpyrrole **2a** were studied (Scheme 3). In addition to **1a**, aliphatic alkynes such as 3-phenyl-1-propyne **1b** and cyclohexylacetylene **1c** were converted smoothly to corresponding branched α,β-unsaturated ketone **3b** and **3c** in good yields and regioselectivities. Increasing the steric bulk of the terminal alkyne still led to good branched selectivity of product **3d** in moderate yield (70% yield, 87% *b*-selectivity). Aromatic alkynes like phenylacetylene reacted smoothly and furnished an excellent yield and *b*-selectivity of the desired product **3e** (88% yield and 99% *b*-selectivity). Alkynes containing halogen and nitrile group were also efficiently converted into the desired products **3f** and **3g** with good regioselectivities. Notably, when a conjugated enyne was used, the double bond remained intact and only the triple bond was selectively carbonylated to the branched ketone **3h** in 81% yield with 99% *b*-selectivity. In addition to terminal alkynes, different internal alkynes were investigated in this transformation as well. The symmetrical alkyl and aryl alkynes underwent efficient carbonylation to afford the corresponding α,β-unsaturated ketones **3i** and **3j** with high stereoselectivity. The carbonylation of an unsymmetrical alkyne, methyl phenylpropiolate, gave the product **3k** in 56% yield with 99% *E*-selectivity. Remarkably, 1,7-octadiyne also reacted smoothly and gave the dicarbonylation product **3l** in moderate yield. To

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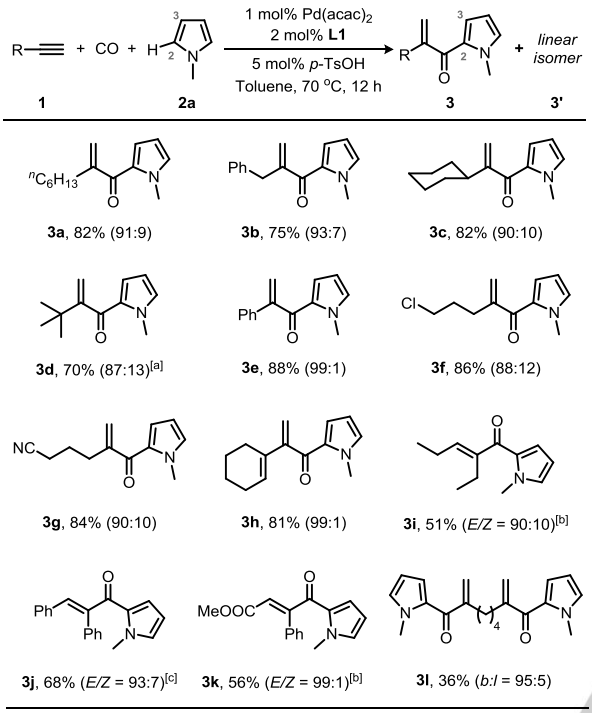
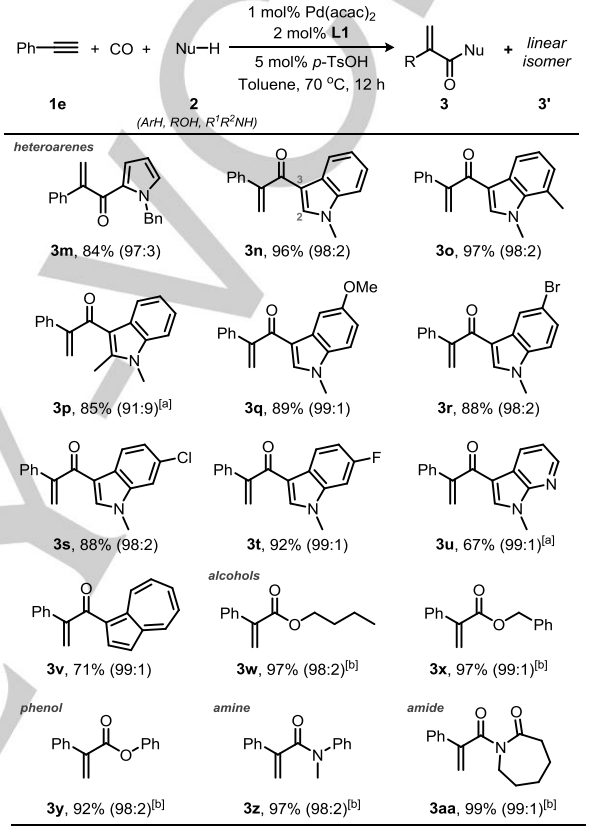
note, all the C-H carbonylation reactions preferentially occurred at C2 position on the pyrrole.



Scheme 3. Markovnikov-selective carbonylation with different alkynes. Reaction conditions: alkyne **1** (1.0 mmol), *N*-methylpyrrole **2a** (0.5 mmol), $Pd(acac)_2$ (1.0 mol%), **L1** (2.0 mol%), *p*-TsOH (5.0 mol%), CO (40 bar), toluene (1.0 mL), 70 °C, 12 h. In each case, the yield of isolated compound **3** is given, and the number in the parenthesis indicates the **3/3'** ratio determined by GC analysis. [a] Reaction at 90 °C. [b] Reaction at 100 °C for 20 h. *E/Z* ratio is determined by GC analysis. [c] Reaction at 90 °C for 20 h. *E/Z* ratio is determined by GC analysis.

Next, we employed structurally diverse heteroarenes as nucleophiles (Scheme 4). For example, benzyl (Bn) protected pyrrole also gave a branched selective carbonylation product **3m** in excellent yield.[15] Due to the importance of substituted indoles it is exciting that *N*-methylindole is a suitable substrate to afford the C3-carbonylated ketone in high yield and regioselectivity (**3n**, 96% yield, 98% *b*-selectivity). Exploring various indole derivatives, we found that substituents including –Me (**3o** and **3p**), –OMe (**3q**), –Br (**3r**), –Cl (**3s**) and –F (**3t**) at different positions on the indole nucleus are all compatible with this catalyst system. The desired Markovnikov products were obtained exclusively at C3 position in 85%–97% yields. Moreover, pyridine-containing scaffold **2u** also worked well under similar conditions to give the corresponding carbonylative product **3u** in moderate yield (67% yield). Interestingly, even azulene led to a good yield of 71 % for **3v** owing to its high nucleophilicity.

To demonstrate the generality for this catalyst, alkoxy- and aminocarbonylations with diverse *O*- and *N*-containing nucleophiles were investigated. For example, carbonylation of phenylacetylene with 1-butanol and benzyl alcohol led to the corresponding branched esters **3w** and **3x** efficiently. Additionally, phenol also furnished the desired alkoxycarbonylation product **3y** in excellent yield and branched selectivity. As an example of amine as nucleophile, *N*-methylaniline worked well and the desired product **3z** was afforded in high isolated yield and selectivity. Last but not least, a less nucleophilic substrate, such as caprolactam also reacted smoothly to give the synthetically interesting imide **3aa** in 99% yield and *b*-selectivity.



Scheme 4. Markovnikov-selective carbonylation with various nucleophiles: heteroarene, alcohol, phenol, amine and amide. Reaction conditions: phenylacetylene **1e** (1.0 mmol), nucleophile **2** (0.5 mmol), $Pd(acac)_2$ (1.0 mol%), **L1** (2.0 mol%), *p*-TsOH (5.0 mol%), CO (40 bar), toluene (1.0 mL), 70 °C, 12 h. In each case, the yield of isolated compound **3** is given, and the number in the parenthesis indicates the **3/3'** ratio determined by GC analysis. [a] Reaction at 90 °C. [b] Reaction at 100 °C.

Finally, we were interested in demonstrating the usefulness of our products as intermediates in organic synthesis. Starting from commercially available alkynes and heteroarenes, the substituted cyclopentanones (**4a** to **4f**) can be readily accessed in a "one-pot" process when our carbonylation reaction is combined with Nazarov cyclization[16] (Scheme 5). To the best of our knowledge, this step-economical annulation process allows for the most effective generation of such polycyclic ring products.

In addition, the α,β-unsaturated ketone can be further converted to γ-keto ester **5** in high yield via palladium catalyzed alkoxycarbonylation (Scheme 6).[3f] Notably, **5** is an analogue of Levulinic ester, which can be similarly used for further valorization.[17]

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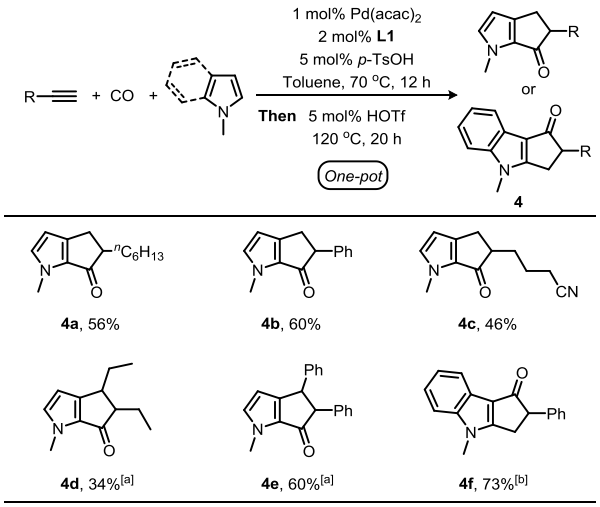
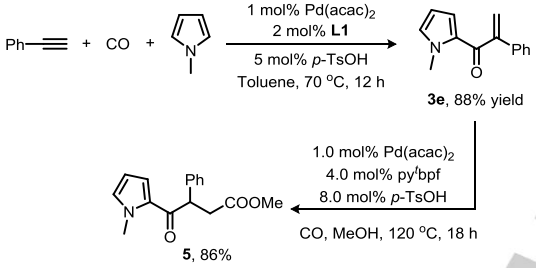


Scheme 5. Synthetisis of substituted cyclopentanones in one-pot. [a] at 90 °C in step 1. [b] with 10 mol% *p*-TsOH instead of HOTf in step 2.



Scheme 6. Synthetisis of γ-keto ester.

In summary, we developed the first palladium catalyst system for a Markovnikov-selective carbonylation of alkynes with heteroarenes. By applying the novel ligand **L1** (bis(2-(diphenylphosphanyl)-1H-pyrrol-1-yl)methane), a wide range of unactivated alkynes and heteroarenes as well as other nucleophiles, such as alcohol, phenol, amine and amide, are efficiently transformed into the corresponding branched α,β-unsaturated products in good yields and often with high regioselectivity. The general applicability of this methodology is demonstrated by "one-pot" synthesis of polycyclic ring products. In view of the easy availability of the substrates, the efficiency, and the good regioselectivity, this novel catalyst system is expected to complement the current methods for carbonylations in homogenous catalysis and organic synthesis.

Acknowledgements

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Keywords: diphosphine • carbonylation • Markovnikov-selective • alkyne • ketone

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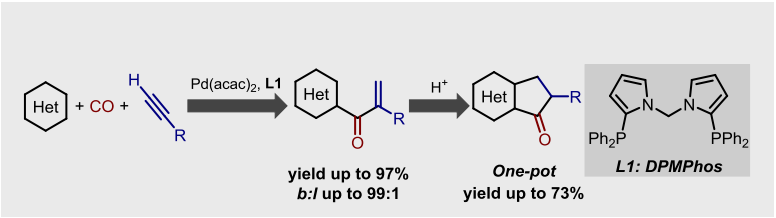

It's a new *cat*: The ligand L1 (bis(2-(diphenylphosphanyl)-1H-pyrrol-1-yl)methane) allows for a general palladium-catalyzed carbonylation of unactivated alkynes with heteroarenes. The reaction proceeds smoothly to give the corresponding branched α,β-unsaturated ketones in good yields (up to 97%) and often with high Markovnikov-selectivity (*b:l* up to 99:1).

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